

- (21) Application No. 48088/77 (22) Filed 18 Nov. 1977 (19)
(31) Convention Application No. 2652603 (32) Filed 19 Nov. 1976 in
(33) Fed. Rep. of Germany (DE)
(44) Complete Specification Published 10 Jan. 1979
(51) INT. CL.² C08J 3/20 //
C09D 11/12
(52) Index at Acceptance
C3L DH
(72) Inventors: WILHELM SCHUMACHER
HANS GRÄF



(54) PRODUCTION OF COATING
COMPOSITIONS FOR CARBON PAPERS

(71) We, DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT VORMALS ROESSLER a body corporate organised under the laws of Germany of 9 Weissfrauenstrasse, 6 Frankfurt Main 1, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a process for the production of pigment-containing coating compositions for carbon papers.

The starting paper for flimsy carbon papers may be so-called carbon silk for example. The paper consisting of rag or cellulose with a weight per unit area of from 10 to 20 g/cm² should be tough, non-porous and free from nodes. Pure cellulose starting papers with weights per unit area of from 30 to 40 g/cm² are used for the production of special carbon papers, *inter alia* for accounting machines. The starting papers are coated with pigments (for example carbon black, milori blue or paraffin-carbon black emulsions) which are mixed with waxes, resins or oils. In order to prevent it from curling up in use, the paper is generally backed with a layer of wax or plastic. Individual sheets of so-called "reusable carbon paper", which is the most widely used, are required to give clear, legible copies and to lend themselves to repeated use. So-called "non-reusable carbon papers", which are only used once, are intended for pads or printed forms. Thicker special types are used for duplicating papers, for spirit carbons and for accounting machines.

It is known that pigment-containing coating compositions for carbon papers which are applied to the starting paper by spread-coating or printing can be produced by processing the composition in the melt or in an organic solvent phase.

Unfortunately, conventional processes are attended by the disadvantage of a high energy consumption for producing and maintaining the melt or for extracting, recovering and eliminating the solvents which are generally damaging to health.

An object of the present invention is to provide a process for the production of pigment-containing coating compositions for carbon papers in whose case it is not necessary to work either in the melt or in an organic solvent phase.

The present invention provides a process for the production of a pigment-containing coating composition for carbon papers which comprises intensively mixing an aqueous wax emulsion with an aqueous carbon black dispersion and vegetable, animal or mineral oil, a pyrogenic silica optionally being added during mixing.

The mixture components excluding pyrogenic silica may be mixed with one another in a ratio of from 50:30:40 to 50:60:10. In one preferred embodiment of the process according to the invention, the mixture components may be mixed with one another in a ratio of 50:50:20. A mixture of bone oil, olein and castor oil in a ratio of 40:40:20 may also be added as oil to the mixture as a whole.

By virtue of the process according to the invention, it is possible to produce pigment-containing coating compositions for carbon papers without having to use an energy-consuming melt or physiologically dangerous organic solvents.

In the context of the invention, the term wax is generically used for a number of natural or synthetic substances which generally have the following properties: at 20°C. kneadable, solid or hard and brittle, coarsely to finely crystalline, transparent to opaque, but not glass-like, above 40°C melting without decomposition and non-stringy, highly

temperature-dependent consistency and solubility, polishable under light pressure (cf. Ullmanns Enzyklopadie der technischen Chemie, Vol. 18, 3rd Edition, pages 262 to 305/1967).

- 5 The addition of pyrogenic silica can improve the stability and storability of the pigment-containing coating compositions and, in addition, provides for greater clarity and depth of colour of the carbon copies. The pyrogenic silica may be added in quantities of from 0.1 to 3% by weight, based on the mixture as a whole.

The process according to the invention is illustrated by the following Examples:

EXAMPLE 1

- 10 Polyethylene wax emulsion:
120.0 parts by weight of wax PAD 521 (Hoechst)
24.0 parts by weight of olein
10.0 parts by weight of KOH
8.0 parts by weight of triethanolamine

- 15 420.0 parts by weight of water.
Triethanolamine and KOH are stirred into the heated wax-olein melt. The mixture is then stirred into boiling water. On completion of emulsification, the mixture is cooled to room temperature.

The polyethylene wax PAD 521 used had the following characteristics:

- 20 Drip point DGF-M-III 3 (57):
Solidification point DGF-M-III 4 a (63):
Acid number DGF-M-IV 2 (57):
Saponification number DGF-M-IV 2 (57):
25 Density DGF-M-III 2 a (57):
Penetration number 100 g/25°C/5s:
Colour:

98 - 102°C
86 - 90°C
14 - 18
20 - 35
0.93 - 0.95
4 - 6
almost white

The emulsifier system is ionic.

EXAMPLE 2

- 30 Mixtures of the polyethylene wax emulsion according to Example 1 with various aqueous carbon black dispersions and mineral oil:

- 35 2.1 50.0 parts by weight of polyethylene wax emulsion according to Example 1
50.0 parts by weight of carbon black dispersion AGK 45/P 200 (A product of Degussa)
20.0 parts by weight of Shell oil 3107 ('Shell' is a Trade Mark)
- 40 2.2 50.0 parts by weight of polyethylene wax emulsion according to Example 1
50.0 parts by weight of carbon black dispersions AN3AG 20/160 (Degussa)
20.0 parts by weight of Shell oil 3107
- 45 2.3 50.0 parts by weight of polyethylene wax emulsion according to Example 1
50.0 parts by weight of Derussol 345
20.0 parts by weight of Shell oil 3107
- 50 2.4 50.0 parts by weight of polyethylene wax emulsion according to Example 1
50.0 parts by weight of carbon black dispersion AN3AG 30/300 (Degussa)
20.0 parts by weight of Shell oil 3107
- 55 2.5 50.0 parts by weight of polyethylene wax emulsion according to Example 1
50.0 parts by weight of Derussol P 130
20.0 parts by weight of Shell oil 3107

EXAMPLE 3

Mixtures of the polyethylene wax emulsion according to Example 1 with an aqueous carbon black dispersion and various oils.

- 3.1 50.0 parts by weight of polyethylene wax emulsion according to Example 1
50.0 parts by weight of carbon black dispersion AGK 45/P 200 (Degussa)
20.0 parts by weight of spindle oil 33 cSt. (CORAY 36-Esso)
- 3.2 same as 3.1, except that the oil component consists of a mixture of 40% of bone oil,
40% of olein and 20% of castor oil
- 3.3 same as 3.1, except that the oil component is castor oil
- 3.4 same as 3.1, except that the oil component is bone oil

EXAMPLE 4

Mixtures of standard commercial-grade wax emulsions with an aqueous carbon black dispersion and mineral oil

- 4.1 50.0 parts by weight of Staprint D-FPG-947 N (Hendricks + Sommer)
50.0 parts by weight of carbon black dispersion AGK 45/P 200 (Degussa)
20.0 parts by weight of spindle oil 33 cSt.
- 4.2 50.0 parts by weight of Poligen PE (BASF - 'Poligen' is a Trade Mark)
50.0 parts by weight of carbon black dispersion AGK 45/P 200 (Degussa)
20.0 parts by weight of spindle oil 33 cSt.
- 4.3 50.0 parts by weight of HORDAMER PE O1 (Hoechst)
50.0 parts by weight of carbon black dispersion AGK 45/P 200 (Degussa)
20.0 parts by weight of spindle oil 33 cSt.
- 4.4 50.0 parts by weight of VAE dispersion LT 411 (Wacker)
50.0 parts by weight of carbon black dispersion AGK 45/P 200 (Degussa)
20.0 parts by weight of spindle oil 33 cSt.

EXAMPLE 5

Mixture of a standard commercial grade wax emulsion, an aqueous carbon black dispersion, a mineral oil and an addition of AEROSIL 200. ('Aerosil' is a Trade Mark).

- 5.1 100.0 parts by weight of the mixture according to Example 4.2
1.0 by weight of pyrogenic silica

The pyrogenic silica has the following physical-chemical characteristics:

BET-surface	m ² /g	200 ± 25
Average primary particle size	micrometers	12
Apparent density		
normal product	g/l	approx. 60
compressed product (addition "V")	g/l	approx. 120
Bulking value (according to DIN 53 194)		
normal product	ml/100 g	approx. 1700
compressed product (addition "V")	ml/100 g	approx. 1000
Drying loss (according to DIN 53 198, method A) 2 hours at 105°C	%	<1.5

	Ignition loss*) (according to DIN 52 911) 2 hours at 1000°C	%	<1		
5	pH-value (according to DIN 53 200) in 4% aqueous dispersion		3.6 - 4.3	5	5
	SiO ₂ *)	%	>99.8		
	Al ₂ O ₃	%	< 0.05		
	Fe ₂ O ₃	%	< 0.003		
10	TiO ₂	%	< 0.03	10	10
	HCl	%	< 0.025		
	Grit according to Mocker (DIN 53 580)	%	< 0.05		
15	Package size (nett) normal product	kg	10	15	15
	compressed product (addition "V")	kg	20		
	*) (based on the substance dried for 2 hours at 105°C.				
20	Characteristics of the mixture ingredients used:			20	20
	Staprint DFPG-947 N (polyethylene was lysol, a product of Hendricks + Sommer, Kunstharze KG)				
25	Finely disperse, aqueous non-ionic dispersion based on oxidised polyethylene waxes			25	25
	Solids	32 ± 1%			
	pH-value	9.5 - 10.5			
	Specific gravity at 25°C	0.98 kg/dm ³			
30	Viscosity at 25°C	below 200 cP		30	
	Emulsifier system	non-ionic			
	POLIGEN PE (BASF)				
35	Solids content	40 ± 1%		35	
	pH-value	9.5 - 11			
	Viscosity at 25°C (C 87) (Ubbelohde capillary viscosi-meter)	<50			
40	Density at 20°C	0.96 - 0.98		40	
	Average particle size	0.10 - 0.15 micron			
	Average molecular weight of the solids (according to viscosity measurement)	16.000 - 20.000			
45				45	
	HORDAMER PE 01 (Hoechst)	corresponding to Poligen PE			
	VAE-dispersion LT 411 (Wacker) (aqueous dispersion of a copolmer)				
50	Solids content	43%		50	
	Polyethylene content of the solids	40%			
	Polyvinylacetate content of the solids	60%			
55	The bone oil used in Examples 1 to 5 corresponds to the definition in Rompp's-Chemie-Lexikon, 6th Edition, column 3291: Franchh'sche Verlagsbuchhandlung Stuttgart.			55	
	The castor oil used in Examples 1 to 5 corresponds to the definition in Rompp's Chemie-Lexikon, column 5469.				
	The spindle oil used in Examples 1 to 5 corresponds to the definition in Rompp's Chemie-Lexikon, column 5714.				
60	The carbon black dispersions used in Examples 1 to 5 may be characterised as follows:			60	
	Carbon black dispersion AGK 45/P 200: aqueous dispersion with non-ionic wetting agent and 45% of furnace black (average primary particle size 46 nm).				
65	Carbon black dispersion AN 3 AG 20/160: aqueous dispersion with non-ionic wetting agent and 20% of gas black (average primary particle size 20 nm).			65	

Derussol 345: aqueous carbon black dispersion with anion-active wetting agent and 45% of furnace black (average primary particle size 27 nm).

Carbon black dispersion AN 3 AG 30/300: aqueous dispersion with non-ionic wetting agent and 30% of furnace black (average primary particle size 27 nm).

5 Derussol P 130: aqueous carbon black dispersion with non-ionic wetting agent and 20% of gas black (average primary particle size 25 nm).

WHAT WE CLAIM IS:-

10 1. A process for the production of a pigment-containing coating composition for carbon papers, which comprises intensively mixing an aqueous wax emulsion with an aqueous carbon black dispersion and vegetable, animal or mineral oil.

2. A process as claimed in Claim 1, wherein the mixture components are mixed with one another in a ratio of from 50:30:40 to 50:60:10.

3. A process as claimed in Claim 2, wherein the mixture components are mixed with one another in a ratio of from 50:50:20.

15 4. A process as claimed in any of Claims 1 to 3, wherein pyrogenic silica is added during mixing.

5. A process as claimed in Claim 4, wherein the pyrogenic silica is added in an amount of 0.1 to 3% by weight based on the mixture as a whole.

20 6. A process for the production of a pigment-containing coating composition for carbon papers substantially as described with particular reference to any of Examples 2 to 5.

7. A pigment-containing coating composition for carbon papers when produced by a process as claimed in any of Claims 1 to 6.

25 ELKINGTON & FIFE,
Chartered Patent Agents,
High Holborn House,
52/54 High Holborn,
London WC1V 6SH.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.